



1 **A European map of groundwater pH and calcium**

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54 **Abstract.** Water resources and associated ecosystems are becoming highly endangered due to

55 ongoing global environmental changes. Spatial ecological modelling is a widely used tool for

56 understanding the past, present and future distribution and diversity patterns in groundwater-

57 dependent ecosystems, such as fens, springs, streams, reed beds or wet grasslands. Still, the

58 lack of detailed water chemistry maps prevents their reasonable use on continental and global

59 scales. Being major determinants of biological composition and diversity of groundwater-



60 dependent ecosystems, groundwater pH and calcium are of utmost importance. Here we
61 developed the up-to-date European map of groundwater pH and Ca, based on 7,577
62 measurements of near-surface groundwater pH and calcium distributed across Europe. In
63 comparison to the existing European groundwater maps, we included a several times larger
64 number of sites, especially in the regions rich in spring and fen habitats, and filled the apparent
65 gaps in Eastern and Southeastern Europe. We used Random Forest models and regression
66 kriging to create continuous maps of water pH and calcium at the continental scale, which is
67 freely available also as a raster map (Hájek et al. 2020; 10.5281/zenodo.4139912). Lithology
68 had higher importance than climate for both pH and calcium. The previously recognised
69 latitudinal and altitudinal gradients were rediscovered with much refined regional patterns, as
70 associated with bedrock variation. For ecological models of distribution and diversity of
71 groundwater-dependent, but also other terrestrial, ecosystems, the new map is more suitable
72 than previously used maps of soil pH, unlike which it mirrors bedrock chemistry more than
73 vegetation-dependent soil processes.

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78 **1. Introduction**

79 The Earth system is currently undergoing unprecedented changes in climate, global
80 biogeochemical cycles, and land use, resulting in biodiversity loss (Ceballos et al. 2017, Song et



81 al. 2018, Blowes et al. 2019, Brondizio et al. 2019). Freshwater systems belong to the most
82 endangered habitats (Cantonati et al. 2020a, Tickner et al. 2020) and, among them,
83 groundwater-dependent ecosystems, such as fens and springs, hold primacy (Janssen et al.
84 2016, Chytrý et al. 2019, Hájek et al. 2020). Species composition and richness of spring systems
85 are generally governed by water pH and calcium concentration (Ca^{2+}), which are highly variable
86 at different spatial scales (Malmer 1986; Rydin and Jeglum 2013; Peterka et al. 2017; Horsáková
87 et al. 2018; Cantonati et al. 2020a,b). Therefore, understanding the spatial patterns in
88 groundwater pH and Ca^{2+} is important not only for general geochemical knowledge and for
89 water resource management, but to the same extent for the conservation of freshwater
90 systems and associated biodiversity.

91 In Earth and biodiversity sciences, ecological modelling is a widely used tool for
92 understanding the distribution and diversity patterns of ecosystems and habitats, and for
93 predicting their future development under global change. Ecological models usually incorporate
94 environmental or historical predictors extracted from thematic maps (Jiménez-Alfaro et al.
95 2018a, Večeřa et al. 2019, Divíšek et al. 2020), including soil properties for terrestrial
96 ecosystems (Hengl et al. 2017). However, soil parameters as soil pH contribute negligibly to the
97 models for groundwater-dependent habitats, even for those strongly controlled by pH and Ca^{2+} ,
98 such as base-rich fens (Jiménez-Alfaro et al. 2018b). This is due to a poor correlation between
99 groundwater chemistry and pH or Ca^{2+} in soil, disrupted mainly by mineral leaching or
100 accumulation of organic matter in soil. For this reason, there is a strong need to produce maps
101 for groundwater pH and Ca^{2+} concentration at the European scale that would allow producing



102 the continental-scale ecological models useful for enforcing conservation strategies in
103 groundwater-dependent habitats.

104 In spite of important mapping efforts of groundwater (Duscher et al. 2015) and karst
105 aquifers (Chen et al. 2017) at the European and global level, the only available European-scale
106 maps of groundwater pH and Ca^{2+} concentration are those included in the FOREGS Geochemical
107 Atlas of Europe (Salminen et al. 2006). These maps are based on 808 stream-water
108 measurements distributed relatively equally across Europe. However, they show a large gap in
109 Eastern and Southeastern Europe (Romania, Bulgaria, Belarus, Russian Federation, Ukraine,
110 Moldova, Serbia, Kosovo, Montenegro, Bosnia and Herzegovina, Northern Macedonia). In
111 addition, the maps are constructed based on insufficient data density in some areas rich in
112 different groundwater-dependent ecosystems, but heterogeneous in terms of lithology (the
113 Alps, the Carpathians, Bohemian Massif, the Cantabrian Mountains and the Pyrenees, and some
114 regions of Fennoscandia). We therefore aimed at substantial improvement of the existing data
115 by creating a database with field data measurements across the entire European continent, and
116 at creating a model-based map representing major patterns of groundwater pH and Ca^{2+}
117 concentration at local and continental scales. Our data will allow better understanding of the
118 patterns and causes of groundwater conditions in freshwater systems, and strongly improve
119 the databases for European-scale modelling of the biodiversity in groundwater-dependent and
120 related ecosystems.

121

122 2. Methods



123 *Data collection*

124 We assembled the data set of pH and Ca²⁺ (or electrical conductivity in $\mu\text{S}\cdot\text{cm}^{-1}$ at 20 °C;
125 hereinafter abbreviated as EC) measurements in groundwater, covering the whole of Europe,
126 with a greater density in the regions rich in endangered groundwater-dependent ecosystems
127 such as springs and fens. We excluded most of Ukraine and European part of Russian
128 Federation, because of large data gaps in these areas. We considered all types of shallow
129 groundwater systems, especially spring, spring-fen, and stream water. The core of our data set
130 is formed by unpublished pH and Ca²⁺ or EC data sets of co-authors (3,618 sites); some of them
131 processed in ecological papers without presenting original pH and Ca²⁺ data (Hájková et al. 2006,
132 2008; Hájek et al. 2008; Sekulová et al. 2013; Plesková et al. 2016; Horsáková et al. 2018;
133 Šímová et al. 2019). The second most important source were vegetation databases registered in
134 GIVD (Dengler et al. 2011; Table 1) and EVA (Chytrý et al. 2016), from where 1,160
135 measurements from freshwater habitats were obtained. Both unpublished data and data from
136 vegetation databases were filtered using original information or metadata of the sources in a
137 way that only data from spring-fed fens and springs were considered. The data from
138 ombrotrophic bogs and clearly topogenic fens (mainly terrestrialised lakes) were omitted
139 because their water chemistry is governed by the decomposition of organic matter,
140 atmospheric humidity and deposition, algal photosynthesis (Kann and Smith 1999), and biotic
141 processes such as cation exchange capacity of mosses (Clymo 1963, Soudzilovskaia et al. 2010,
142 Vicherová et al. 2015), rather than by bedrock chemistry. We also obtained data from public
143 data sets from national environmental and nature conservation agencies of Germany, Slovenia
144 and Bulgaria (1081 sites; see Table 1), data from FOREGS Geochemical Atlas of Europe



145 (Salminen et al. 2006; 808 sites) and literature data based on our gap-oriented excerption (883
146 sites; Table 1); most data came from Hinterlang (1992), Tanneberger et al. (2011), Eades et al.
147 (2018), Kadūnas et al. (2017) and Savić et al. (2017).

148

149 **Table 1.** Data sources. The name abbreviations are explained in the team list or
150 acknowledgements.

151



I. Vegetation databases.

<i>name</i>	<i>n</i>	<i>GIVD code</i>	<i>custodian</i>
European Mire Vegetation Database (EMVD)	510	GIVD EU-00-022	T.P.
National Vegetation Database of Denmark	373	EU-DK-002	J.E.M.
Britain_nvcd	224	GIVD EU-GB-001	J.R.
Balkan Vegetation Database	27	GIVD EU-00-019	K.V.
Germany_vegmv	19	GIVD EU-DE-001	F.J.
Basque country	7	EU-00-011	I.B.

II. Unpublished data sets

<i>Regions</i>	<i>n</i>	<i>co-authors of the data set</i>
Central and Eastern Europe	1405	Z.P., M.Há., P.H., T.P., D.D., L.S., M.L., J.N., P.P., P.S., A.Š., Y.S., C.B.-N.
Spain	645	A.P-H., E.P-I., B.J-A.
Bulgaria	428	P.H., M.Há., M.Hor.
Fennoscandia	392	M.Há., T.P., D.D., M.Hor., V.H., P.H., T.K., T.T., J.Kap., D.-I.Ø.
Apennines	285	M.T., M.Can., M.Car., S.S., A.P., L.B., R.G.
Europe (cross-taxon research)	281	M.Há., P.H., D.D., M.Hor., V.H.
Balkans except Bulgaria	134	A.D., E.M., J.Kam., P.L., T.P., M.Há., P.H.

III. Public data sets

<i>area and agency</i>	<i>n</i>	<i>provided via</i>
North Rhine-Westphalia (LANUV agency; D)	463	Dr. Dirk Hinterlang, Dr. Sabine Bergmann
Ministry of Environment and Water (BG)	442	Mrs. Rossitza Gorova
Ministry of the Environment (SI)	176	http://www.arso.gov.si/ , assessed 26 February 2019

IV. Geochemical Atlas of Europe

<i>area</i>	<i>n</i>	<i>reference</i>
Europe	808	Salminen et al. 2006

V. Other literature data (gap-oriented excerption)

<i>region and context</i>	<i>n</i>	<i>reference</i>
West-Central European springs	340	Hinterlang 1992
Lithuanian springs	194	Kadūnas et al. 2017
NE England	111	Eades et al. 2018
N Germany	58	Tanneberger et al. 2011
Central Bosnia	50	Savić et al. 2017
Western Bohemian mineral springs (CZ)	28	Laburdová and Hájek 2014
Scotland	24	Gorham 1957
Eastern Bosnia	20	Kamberović et al. 2019



Switzerland (mires)	14	Lamentowicz et al. 2010
British and French travertines	13	Pentecost and Zhaohui 2002
NW Poland (mires)	8	Lamentowicz and Mitchell 2005
Western Balkans	6	Ridl et al. 2018
Kosovo	5	Kelmendi et al. 2018
SE Croatia	4	Terzić et al. 2014
Kosovo (Rugova)	3	Lajçi et al. 2017
Serbia	3	Čirić et al. 2018
NE Croatia	1	Špoljar et al. 2011
SE Croatia (Krčić)	1	Kolda et al. 2019

152

153 In total, we collected 7,577 samples (Table 1). A part of the samples, however,
154 represented repeated measurements conducted in the same site, especially in public data sets.
155 Some samples from other data sets (vegetation databases, literature data) shared the same
156 coordinates and site name or code, suggesting repeated measurements as well. We therefore
157 averaged repeated measurements from the same sampling spots. We further deleted samples
158 whose coordinates were obviously erroneous, such as those in oceans. These steps reduced the
159 number of samples to 6,561, out of which 6,459 samples contained information on water pH
160 value and 5,927 samples contained information about EC of water or Ca²⁺ concentration. Out of
161 these 5,927 samples, 2,988 samples had directly measured both Ca²⁺ and EC (μS.cm⁻¹ at 20 °C),
162 and for the remaining 2,939 samples we estimated Ca²⁺ concentration by EC of water.

163

164 *Imputation of missing Ca²⁺ values by EC of water*

165 For imputation of Ca²⁺ values based on EC, we first aimed at constructing a simple imputation
166 equation based on the well-known correlation between EC and Ca²⁺ concentration in springs
167 and fens (Sjörs & Gunnarsson 2002, Plesková et al. 2016). In our data set of 2,988 samples, as



168 well as in its regional subsets, this relationship was strongly governed by EC values above ca
169 1,000 $\mu\text{S}\cdot\text{cm}^{-1}$, although they formed only a small part of the data set (4.7% of the data set; 139
170 samples). In the EC range 1,000-10,000 $\mu\text{S}\cdot\text{cm}^{-1}$ (an outlier of 17,000 $\mu\text{S}\cdot\text{cm}^{-1}$ was omitted), the
171 correlation between water EC and Ca^{2+} concentration was not statistically significant ($r = 0.15$, P
172 = 0.07). The problem of high EC values governing the regression model was the most apparent
173 in the public data sets. In the data set of Bulgarian Ministry of Environment, weak correlation
174 between EC and Ca^{2+} persisted even when EC values above 1000 were omitted (Supplementary
175 Figure 1). This database further contains many samples which are not near-surface samples
176 that were measured in other datasets. We therefore finally decided (1) not to include the
177 database of Bulgarian Ministry of Environment into the imputation model, and (2) limit the
178 gradient of EC to 1,000 $\mu\text{S}\cdot\text{cm}^{-1}$. We further omitted a few samples from ophiolite (Kamberović
179 et al. 2019) where high EC occurred despite low Ca^{2+} . The resulting data set of 2,319 samples
180 nevertheless still showed some samples with suspiciously high or low Ca^{2+} concentration relative
181 to EC (Supplementary Figure 2), suggesting either the effect of other ions than Ca^{2+} or
182 inconsistent analytical methodology. Because our aim was to create the most accurate
183 imputation model rather than testing the relationship, we removed these outliers. Therefore,
184 we calculated the EC:Ca and Ca:EC ratios and removed outliers, i.e., all points outside the 1.5 x
185 interquartile range. The final imputation model was hence based on 2,062 sites. We performed
186 a null-intercept linear regression (Figure 1) with Ca^{2+} as dependent variable (y) and EC as
187 predictor (x); the resulting equation $y = 0.153x$ was obtained ($R^2 = 0.84$). Based on this
188 equation, we imputed Ca^{2+} concentrations to all samples where only EC was measured. The
189 imputed Ca^{2+} values show a somewhat narrower range (Supplementary Figure 3) than originally

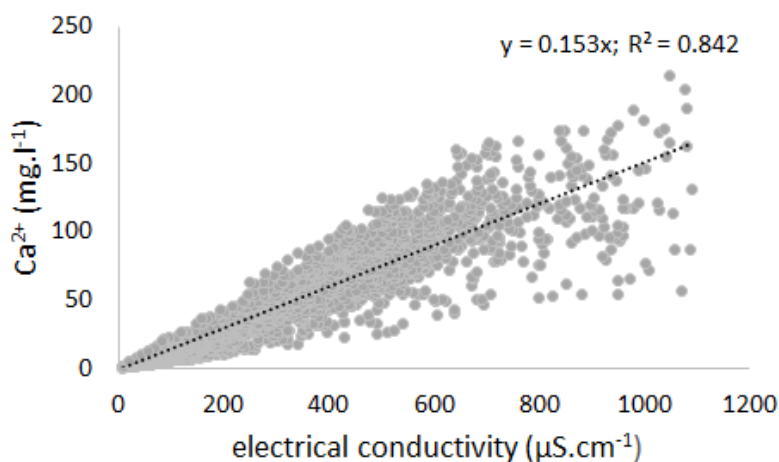


190 measured values. Both subsets show minimum Ca^{2+} value below 1 mg.l^{-1} , but imputed data
191 show lower non-outlier maximum (125.5 mg.l^{-1}) than measured data (197.2 mg.l^{-1}). Absolute
192 maximum value was also lower for the subset with imputed values. Imputation of Ca^{2+} values to
193 all samples, including high-EC ones ($> 1,000 \mu\text{S.cm}^{-1}$), hence did not skew the imputed data to
194 higher values.

195

196 **Figure 1:** The final regression model to impute Ca^{2+} values based on electrical conductivity (EC;
197 $\mu\text{S.cm}^{-1}$; $n = 2,062$

198



199

200 *Geographical modelling*

201 We used our dataset with 6,561 sites with measured groundwater pH and either measured or
202 imputed Ca^{2+} concentrations to model expected values across non-sampled areas.

203 Groundwater-dependent pH (GW-pH) was modeled with 6,459 samples (pH min = 2.20; max =



204 11.32; mean = 6.69); and groundwater-dependent Ca^{2+} (GW-Ca) with 5,927 samples (min =
205 0.15; max = 3567.41; mean = 48.73 mg.l^{-1}). Ca^{2+} values were ln-transformed. All field samples
206 had geographic coordinates assigned from GPS or georeferenced with an accuracy between ca
207 10 (precise field measurements) and 500 m (some database data). We kept the pH outliers; ten
208 values below 3.5 and nine values above 8.8. Even if these values may be suspicious, they largely
209 come from published sources (FOREGS Geochemical Atlas of Europe, British vegetation
210 database). Apart from measurement error, they may be explained by the influence of mineral
211 waters from deep hydrological circulations (e.g., in a spring in the Apennines, very high pH
212 value 11.2 was due to enrichment with sodium and chloride associated with low temperature
213 reaction between meteoric water and ultramafic rocks; Boschetti and Toscani 2008, Boschetti
214 et al. 2013, Segadelli et al. 2017, Cantonati et al. 2020c). These values form only a minor part of
215 the data set and have negligible effect on the results.

216 For each site, we obtained environmental predictors from the thematic GIS maps (see
217 below). For some sites, important predictors were missing in the maps (e.g., sites at far north in
218 the arctic zone, or close to sea or water bodies) and these sites were therefore not included in
219 the final models.

220

221 *Numerical analyses*

222 Numerical analyses were done in R version 3.6.3 (R Core Team, 2020), with the support of
223 ArcGIS 10.2 (ESRI, Redlands, CA) for geoprocessing and map production. We first conducted
224 exploratory analyses to test the Ca and pH prediction ability of different GIS layers related to



225 soil bedrock, climate, and topography. We focused on layers with a complete coverage of
226 Europe with an eastern border from the Black Sea in Turkey to the White Sea in Russian
227 Federation, thus including the regions with a relatively good cover of field measurements
228 (Figure 2). We performed Linear Models for individual variables to select those providing
229 significant relationships and $> 1\%$ of explained variance. A variable for soil pH (measured in
230 water solution) at 15 cm depth for a 250 m grid resolution provided by the soilgrids project
231 (www.soilgrids.org) had the highest explanatory power for GW-pH ($R^2 = 0.22$) and GW-Ca ($R^2 =$
232 0.16). The same results were obtained when using the same variable for 5 or 10 cm depth. We
233 also tested soil estimates from Ballabio et al. (2019), but they provided weaker relationships for
234 both GW-pH ($R^2 = 0.14$ using soil pH as a predictor) and GW-Ca ($R^2 = 0.01$ using soil pH, $R^2 = 0.01$
235 using soil CaCO_3). To account for lithology, we used the lithological groups (litho3 level)
236 included in the polygon layer of the Hydrogeological map of Europe (Duscher et al. 2015) as a
237 categorical variable. We also selected annual precipitation (Bio12) as provided in CHELSA
238 (Karger et al. 2017) to account for precipitation gradients which are expected to influence
239 groundwater regimes. Other variables related to precipitation were highly correlated with
240 annual precipitation (Pearson $r > 0.75$) and omitted. The variables of lithology and soil pH were
241 aggregated to the same grid extent of CHELSA at 1 km resolution, using the dominant unit and a
242 bilinear interpolation, respectively.

243

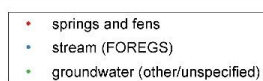
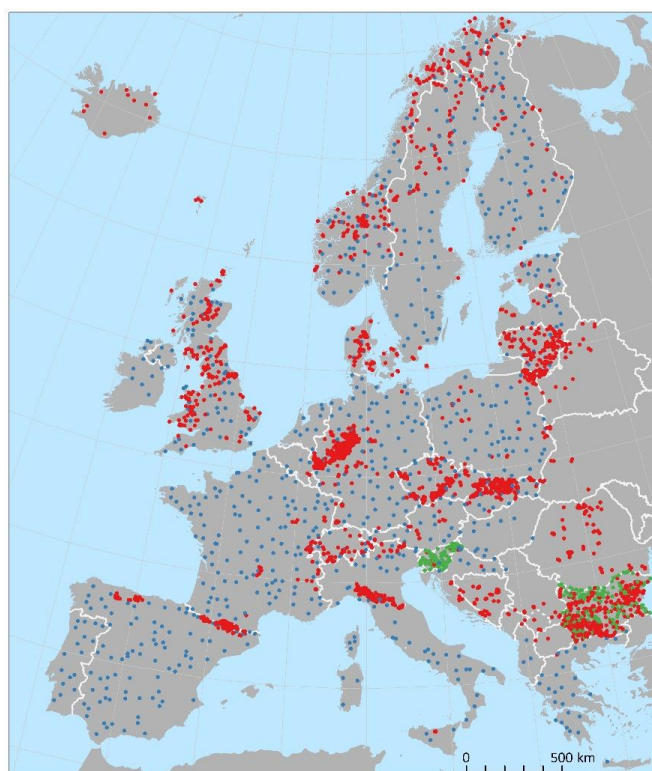
244 **Figure 2.** Spatial distribution of the three groups of calibration data collected for modelling
245 groundwater pH and Ca^{2+} in European fens (original and literature data from springs and fens;
246 data from streams from FOREGS Geochemical Atlas of Europe; other data). Other data include



247 public data from national groundwater monitoring of Bulgaria and Slovenia. For separate maps

248 of pH and Ca²⁺ see Supplementary Figure 5.

249



250

251

252 Spatial predictions were based on regression kriging (RK), a technique that combines a

253 regression model based on explanatory variables with the interpolation of model residuals with

254 ordinary kriging (Hengl et al. 2007; Meng et al. 2013). RK is especially appropriate for modeling

255 soil attributes at medium and large scales, combining the spatial autocorrelation of soil



256 variables with the explanatory power of auxiliary variables (Keskin and Grunwald 2018). We
257 implemented RK with the GSIF R package (Hengl 2020). As the regression component, we
258 computed Random Forests since a preliminary analysis with our data showed better
259 performance than linear models, generalised linear models, or generalised additive models.
260 Random Forests are ensemble learning methods based on decision trees and an internal
261 correction of overfitting, which provide high interpretability and good performance when
262 compared with other algorithms used in soil spatial modeling (Wiesmeier et al. 2011). Another
263 advantage of Random Forests is that they have no requirements for considering the probability
264 distribution of soil variables, fitting complex non-linear relationships for spatial extrapolation
265 (Hengl et al. 2015). We fitted the Random Forests model and the residual variogram for
266 groundwater pH and Ca^{2+} separately using the function `fit.gstatModel()` in GSIF package. Spatial
267 predictions were then computed with the `predict()` function using the model object generated
268 previously and a 5-fold cross-validation. Model evaluation was based on the calculation of the
269 Mean Error (ME) and the Root Mean Squared Error (RMSE) as the differences between
270 predicted and observed values (Keskin and Grunwald 2018; Pham et al. 2019). We compared
271 the relationships between the models for groundwater pH and Ca^{2+} by using a random sampling
272 of 5,000 points to extract cell values and computing a Pearson correlation. To assess regional
273 differences, we correlated values grouped in 25 neighboring cells of each single cell using the
274 `rasterCorrelation()` function in the package `spatialEco`.

275

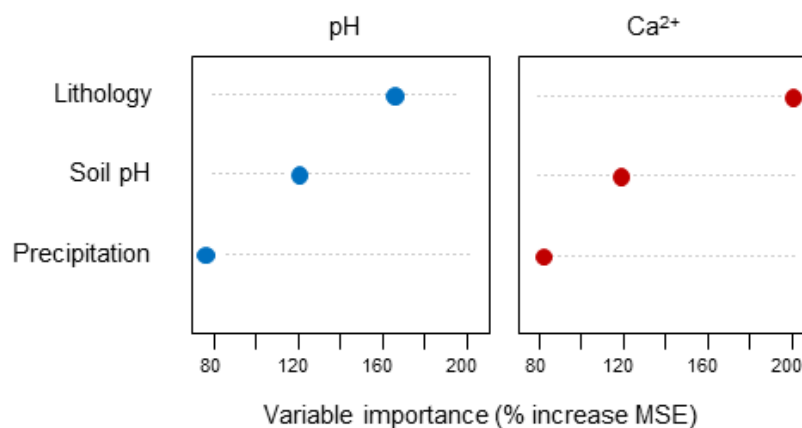
276 3. Results



277 In measured data, ranges and medians of pH and Ca^{2+} concentration was similar across
278 Europe (Supplementary Figure 4), with lowest pH values found in the Atlantic and Iberian
279 regions and highest pH values found in southern Europe except Iberian Peninsula. Lowest Ca^{2+}
280 values were found in boreal Europe, while the highest in Central and Southern Europe. The
281 Random Forest models computed with the lithology, soil pH, and precipitation explained 40%
282 and 55% of the variance for GW-pH and GW-Ca, respectively. Lithology was the variable with
283 the highest importance in both models (Figure 3), although its effect was higher in the model
284 computed for Ca^{2+} than for pH. Conversely, soil pH had higher relative importance in GW-pH
285 than GW-Ca, while precipitation had the lowest contributions in both models.

286

287 **Figure 3.** Variable importance of Random Forest models computed for groundwater pH and
288 Ca^{2+} . MSE = Mean Standard Error.



289

290



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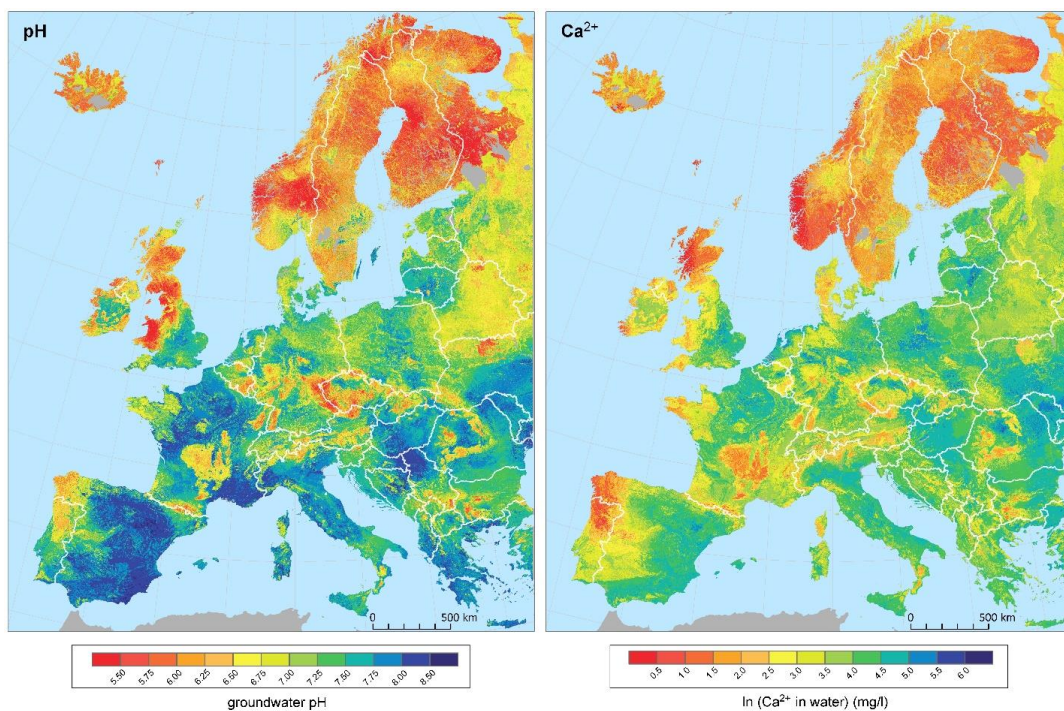
292 When adding the kriging component, model predictions reached 65% and 74% of explained
293 variance for GW-pH and GW-Ca, respectively. The mean values of standard errors (SE; 0.00058
294 for pH; -0.0009 for Ca) and Root Mean Squared Errors (RMSE; 0.588 for pH; 0.690 for Ca) were
295 higher in the models for pH, but in both cases showed low values and accurate predictions, in
296 agreement with their total explained variance.

297 Model predictions for groundwater pH reflected the lowest values in Scandinavia, Iceland,
298 northern UK, and some regions of Central and Eastern Europe (Figure 4). The highest values
299 were predicted in eastern Iberia and many regions of Central and Eastern Europe, although a
300 big part of the study area was dominated by neutral pH values (6 to 7). The spatial patterns for
301 GW-Ca (Figure 4) were rather similar to pH. The overall correlation between the two models
302 was 0.83 (Pearson r , $P < 0.001$), but they showed differences in some regions. This was
303 supported by the spatial correlation computed for each cell (Figure 5), reflecting different
304 magnitudes of correlation across the study area, especially in the eastern Iberian Peninsula and
305 Southeastern Europe.

306

307 **Figure 4.** Model predictions based on Regression Kriging. Note the Ca^{2+} concentration is on ln-
308 scale.

309



310

311



312 **Figure 5.** Spatial correlation between the models computed for groundwater pH and Ca^{2+} .
313 Values show Pearson correlation coefficient computed over every single cell by using a
314 sampling of 25 neighboring cells.



315

316 Discussion

317 3.1. *Spatial patterns in groundwater pH and Ca^{2+} concentration in Europe*



318 As expected, the recent values of water pH and Ca^{2+} concentration are largely shaped by
319 lithology in groundwater-dependent habitats across Europe. Indeed, it has been recognised by
320 regional studies that the distribution of major spring and fen habitats, of which the species
321 composition largely depends on pH and Ca^{2+} , is well determined by bedrock type (Hájek et al.
322 2002, Tahvanainen 2004, Hinterlang 2017, Peterka et al. 2017, Cantonati et al. 2020c). Since the
323 European-scale geological map used here is not precise enough to capture differences in
324 bedrock chemistry within the major geological units that are defined largely by age, the
325 contribution of soil pH in the model probably also reflected lithological variation, as soil pH
326 generally correlates with regional bedrock chemistry (Chadwick and Chorover 2001). On the
327 other hand, soil pH is also affected by climate-dependent pedogenesis, which incorporates a
328 climate-zonal geographical component in this effect (Duchaufour 2012, Maxbauer et al. 2017).
329 Precipitation is another important determinant of groundwater chemistry. Precipitation
330 amount and frequency affect not only flow paths activity and redistribution of groundwater,
331 but also its residence time in the aquifer, impacting carbonate dissolution and precipitation
332 rates (Crossman et al. 2011, Lewandowski et al. 2015, Vystavna et al. 2020). Groundwater with
333 a short transit time (1–3 years) or ‘young water’ (Soulsby et al. 2015) can be particularly
334 sensitive to changes in precipitation amount and frequency. Here, intensive precipitation may
335 reduce an interaction time of groundwater with Ca^{2+} and carbonates deposited in rocks
336 (Fairchild et al. 1994, Segadelli et al. 2017, Cantonati et al. 2020b), resulting in lower
337 concentration of elements in groundwater. In snow-influenced ecosystems, seasonal snowmelt
338 can also modulate the recharge patterns of groundwater. Particularly, the duration of the
339 snowmelt period can impact the occurrence and dynamic of preferential flow, and prolong or



340 reduce the interaction of the seepage with soil and bedrock materials (Mohammed et al. 2019).
341 We therefore suggest that fast hydrological pathways and short transit time driven by
342 snowmelt and precipitation can explain the lowest Ca^{2+} in hyper-oceanic cold regions of SW
343 Norway or W Scotland. It may further lower pH and Ca^{2+} values on windward slopes of high
344 mountains, even if bedrock is moderately calcium-rich.

345 The resulting pattern at the European scale is governed by the strong latitudinal and
346 altitudinal gradients, i.e. decreasing pH and Ca^{2+} northwards, and regionally also towards
347 mountain regions. Although this pattern is well known (Økland et al. 2001, Hájek et al. 2006,
348 Hinterlang 2017, Peterka et al. 2017) and has been captured also by the FOREGS Geochemical
349 Atlas of Europe (Salminen et al. 2006), our improved model provides much finer regional
350 patterns. In Southern Europe, low pH and Ca^{2+} values were modelled in the Pyrenees, the
351 Balkans, SW Corse, and Calabria, i.e. the regions where boreal or endemic types of fen
352 communities occur as relicts (Chytrý et al. 2020). The Alps, the Apennines, the Carpathians, and
353 the Baltic region show a fine-scaled mosaic of alkaline (calcium-rich) and acidic (calcium-poor)
354 groundwater that contributes to the high diversity and conservation value of groundwater-
355 dependent ecosystems, such as fens (Cantonati et al. 2009, 2011, Gerdol et al. 2011, Joosten et
356 al. 2017, Horsáková et al. 2018). The most apparent “acidic island” in Central Europe is located
357 in the SW part of the Bohemian Massif (Czech Republic, Germany), where acidic types of
358 springs and fens are quite frequent and some studies further document anthropogenic
359 acidification on siliceous bedrock in 1970–80s, being re-emerged recently because of extreme
360 climatic events (Kapfer et al. 2012, Schweiger et al. 2015). It is, however, possible that
361 particularly this acidic island is picked out mainly because of the high amount of available data.



362 Clearly, most of Fennoscandia is markedly acidic and calcium-poor mainly due to glacial
363 history. Yet, the model identified small alkaline and calcium-enriched islands in NE and Central
364 Sweden, and NW Norway, which are associated with rare types of calcareous fen and spring
365 communities (Dierssen 1982, Vorren et al. 1999, Udd et al. 2015, Miller et al. 2020). More
366 localised pockets of calcareous habitats are however known from most parts of Fennoscandia
367 that are not recognised with the grain of our European-wide analysis. With our results, the
368 future modelling of diversity and distribution of individual habitat types of groundwater-
369 dependent wetlands will be more reliable, regionally rare habitat conditions can be better
370 recognised, and the disentangling of the climate and pH effects will be more easily feasible.

371

372 3.2. *Persisting data gaps*

373 Although being based on the hitherto most comprehensive field data set, the presented
374 map cannot be considered definitive. Surely there are many pH and EC or Ca^{2+} measurements
375 conducted across Europe that we could not include into the data set because they are hardly
376 accessible. Except for Russian Federation and Moldova, largest gaps still occur in the southern
377 parts of the Pannonian plain (southeastern Hungary, northern Serbia, and western Romania), in
378 SE Belarus, and eastern Ukraine. We dispose of some data from the latter region (Vystavna et
379 al. 2015; Supplementary Table 2), but a large gap in the rest of the data set prevented reliable
380 geospatial modelling. These data might be used in future updates of the map once the gap in
381 Central Ukraine is filled. The lack of data in the Pannonian plain has led to poor correlation
382 between predicted pH and Ca^{2+} values (Fig. 4). Such a poor correlation and sometimes low
383 density of data apply also for some other lowland regions, such as the Danube plain in S



384 Romania, Po valley in Italy and valleys around the Duero, Ebro, and Tagus rivers in Spain. Apart
385 from eutrophication, this result may be caused by the imbalanced distribution of groundwater-
386 dependent habitat types in our data set. Unlike mountain regions, the data for these lowlands
387 were largely taken from the FOREGS Geochemical Atlas of Europe (Salminen et al. 2006) and
388 national groundwater databases, i.e. largely from stream water. Considering the major purpose
389 of our map, the ecological modelling of fens and springs, these regions are generally not as
390 important because of the low number of existing target habitats, as they have largely been
391 transformed to arable land or they are too dry. On the other hand, caution is needed when
392 interpreting the maps in an ecological sense. The extremely high pH (> 8) and Ca^{2+} ($\ln [\text{Ca}^{2+}] > 4$;
393 i.e., $\text{Ca}^{2+} > 55 \text{ mg.l}^{-1}$) values that occur in lowlands visually govern the map, but for ecological
394 differentiation of groundwater-dependent habitats in Europe the differences within the middle
395 part of the gradient, i.e. between pH 5.5 and 7.0, are much more important (Malmer 1986,
396 Wheeler & Proctor 2000, Hájek et al. 2006, Rydin and Jeglum 2013). In any case, our data set is
397 expected to be amended in the future, as more studies will be published and more data will be
398 available. New data will help to improve predictions for those regions with relatively lower
399 sampling effort, and also those with a lithologically heterogeneous landscape. Future updates
400 of the model may also focus at finer spatial resolution (e.g., 100 to 250 m) but this will require
401 to increase the spatial accuracy of the calibration data and the predictor variables.

402 Despite these persisting gaps, our European map of near-surface groundwater pH and
403 EC provides the best solution for modelling the biodiversity of groundwater-dependent
404 ecosystems, especially at the continental or supra-regional scale. We even believe that this map



405 could be more suitable also for ecological modelling of other than groundwater-dependent
406 habitats. It may mirror the bedrock chemistry better than the map of soil pH, because soil pH is
407 a resultant of pedogenetic processes, which are tightly associated with the character of the
408 vegetation cover itself (Miles 1985, Duchaufour 2012).

409

410 **Conclusions**

411 Here, we provide the first European map of groundwater pH and Ca^{2+} content. We collected as
412 even as possible distributed field measurements of water pH and Ca^{2+} or EC from European
413 groundwater-dependent habitats, having high data density in regions rich in endangered
414 groundwater-dependent ecosystems (springs, fens), and used geospatial modelling. The model
415 considered predominantly lithology and soil pH (i.e., variables surrogating bedrock chemistry)
416 and precipitation sum (i.e., residence time of groundwater). Our results also provide a freely
417 accessible map that can be used in any kind of spatial modelling, showing better resolution and
418 fewer gaps than previously published maps. The character of our input data, which are also
419 freely accessible, predetermines our map for being used in ecological modelling to address the
420 distribution and diversity of groundwater-dependent ecosystems and associated species.
421 Moreover, we assume the map will represent the best choice also for other types of earth
422 modeling, because unlike previous maps we included Eastern-European and Balkan countries
423 and considered lithology in geospatial modelling.

424

425 **Data availability**



426

427 The dataset of georeferenced pH and EC measurements and the resulting maps in GIS-
428 compatible format (shapefile) are accessible at www.zenodo.org; doi 10.5281/zenodo.4139912
429 (Hájek et al. 2020).

430

431 **Code availability**

432 No original R code was used; the used codes are cited.

433

434 **Sample availability**

435 No geoscientific samples registered as International Geo Sample Number (IGSN) have been
436 used for the manuscript.

437

438 **Team list**

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448

449 **Author contribution**

450 M.H. and B.J-A. contributed equally to the paper. They conceived the research, collected data

451 and led writing. B.J-A. designed and performed Random Forest and Regression Kriging models.

452 O.H. prepared the input data and final map outputs. All authors provided unpublished data and

453 commented on the manuscript.

454

455 **Competing interests**

456 The authors declare that they have no conflict of interest.

457

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472

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474

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